

Pressure broadening, -shift, speed dependence and line mixing in the ν_3 rovibrational band of N_2O

J. LOOS, M. BIRK AND G. WAGNER

German Aerospace Center (DLR), Remote Sensing Technology Institute, joep.loos@dlr.de

Abstract

In this poster, we report measured air-broadening, -shift, speed dependence and Rosenkranz line mixing parameters for the ν_3 fundamental rovibrational band of N_2O . A Bruker IFS 125HR Fourier transform spectrometer was used with a White-type multipass absorption cell with 46.4 m absorption path length to measure four ambient temperature air-broadened absorption spectra at total pressures ranging from 100 to 1000 mbar. A multispectrum fitting technique was used to retrieve parameters up to $|m|=40$ ($m=J''$ and $m=J''+1$ for the P and R branch, respectively) utilizing the partially correlated quadratic speed-dependent hard collision model including Rosenkranz line mixing. Speed dependence of the broadening parameter as well as line mixing could be observed in the spectra. The broadening parameters are compared to HITRAN2012, where deviations can be ascribed to the influence of neglecting speed dependence effects in spectra analyses when using the Voigt line profile. The line mixing coefficients show a smooth dependence on m .

Measurements

- Bruker IFS 125HR Fourier transform spectrometer
- White-type gas cell
- 0.8 m baselength, directly attached to the spectrometer
- Probe gas preparation in 800 l stainless steel vessel with magnetically coupled stirrer
- Temperature measurement with 8 Pt100 1/10B sensors
- Pressure measurement with mks baratrons & PR4000B
- Sealed off measurements

Spectrum processing

- Used software: OPUS 7.0 by Bruker
- Mertz phase correction, ZFF 2, no apodization
- Probe gas spectra were divided by empty cell low resolution spectra to minimize channelling
- Wavenumber axes calibrated using a factor obtained from a fit of line positions from Doppler broadened pure N_2O measurements

Line parameter retrieval

Software

- Microwindow based multispectrum fitting tool [1]
- pCqSDHC (HTP) Routine by Tran *et al.* [2,3] + Rosenkranz line mixing
- ILS is modelled as sinbox + corrections previously characterized using LINEFIT [4]
- The 100 % level is fitted using a 2nd order polynomial and sinusoidal channelling (where necessary)

1. Fit of column density and temperature

- Single spectrum Voigt fit of position, effective line strength and width
- Fit of number density and temperature for each spectrum with HITRAN2012 [5] as line intensity reference
- > fitted number densities agree within 0.3%
- > fitted temperature 0.4 K lower than readings, hinting at systematic errors in relative intensities in HITRAN2012

2. Multispectrum fit of all measurements

- No visible change in residuals when fitting δ_0 , $\nu_{VC,0}$ and η
- > δ_0 , $\nu_{VC,0}$ and η set to zero
- > fit using the qSDV+LM line shape
- Additional fit using the Voigt+LM and Voigt line shape to investigate the impact of SD and LM separately
- Multiple fitting rounds were performed to correctly account for influence of lines outside the fitted microwindow

Temperature	294 K			
Mixing ratio N_2/O_2	10 ppmv			
Absorption path length	46.4 m			
Pressures (mb)	103.7	205.9	498.2	1000.2
Resolution (cm^{-1})	0.0036	0.0072	0.01	0.01
Signal to noise ratio (rms)	1940	2640	2295	3355
Measurement time (h)	11.1	3.9	1.6	3.3



Parameters of the pCqSDHC (HTP) +LM model

- Pressure broadening and -shift (Γ_0, Δ_0)
- Speed dependence of width and shift (Γ_2, Δ_2)
- Dicke narrowing in the hard collision model (ν_{VC})
- Correlation between velocity-changing and dephasing collisions (η)
- Rosenkranz line mixing (Y)

$$I = \Re(F_{HTP}) + Y \cdot \Im(F_{HTP})$$

F_{HTP} : complex line shape model

$$\Gamma_0 = \gamma_0 P \left(\frac{296K}{T} \right)^n \quad \Delta_0 = \delta_0 P \quad \nu_{VC} = \nu_{VC,0} P \left(\frac{296K}{T} \right)$$

$$\Gamma_2 = \gamma_2 P \left(\frac{296K}{T} \right)^n \quad \Delta_2 = \delta_2 P \quad Y = Y_0 P$$

Results

- Fit using the qSDV+LM model shows lower residuals than fits with Voigt+LM and Voigt
- Fitting $\nu_{VC,0}$ instead of γ_2 gives worse residuals
- Spectra fitted to the noise level for high-J lines
- Remaining structure in the residuals (especially present at high pressures) might be due to the limitations of the Rosenkranz first order perturbation approximation
- W-shaped residuals if SD is neglected (Voigt+LM)
- Obvious deviations (0.4% of peak absorbance) from noise if LM is neglected (Voigt)

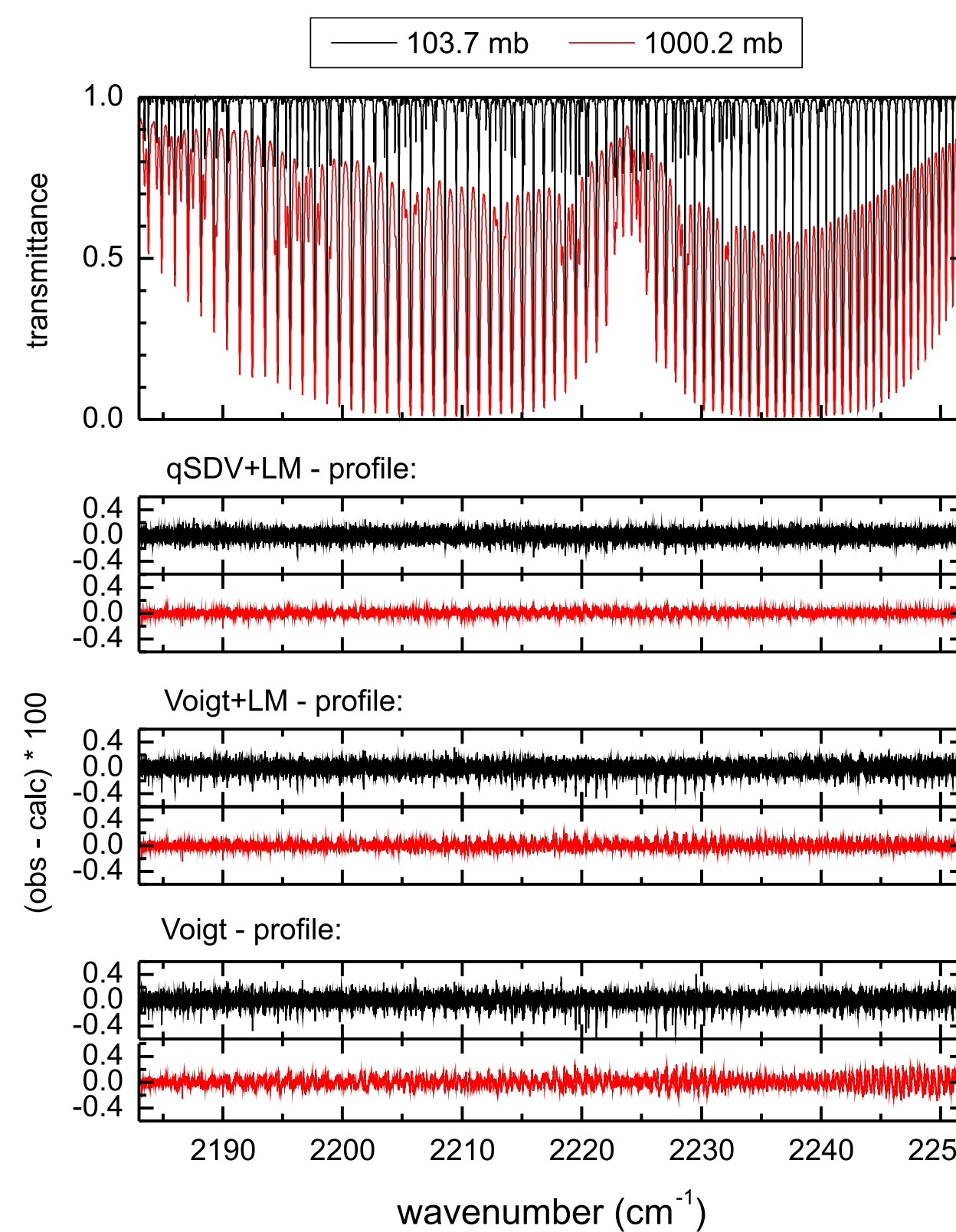


Fig. 1: Measured spectra and concatenated residuals from multispectrum fits of air-broadened N_2O spectra in the ν_3 band using different line shape models.

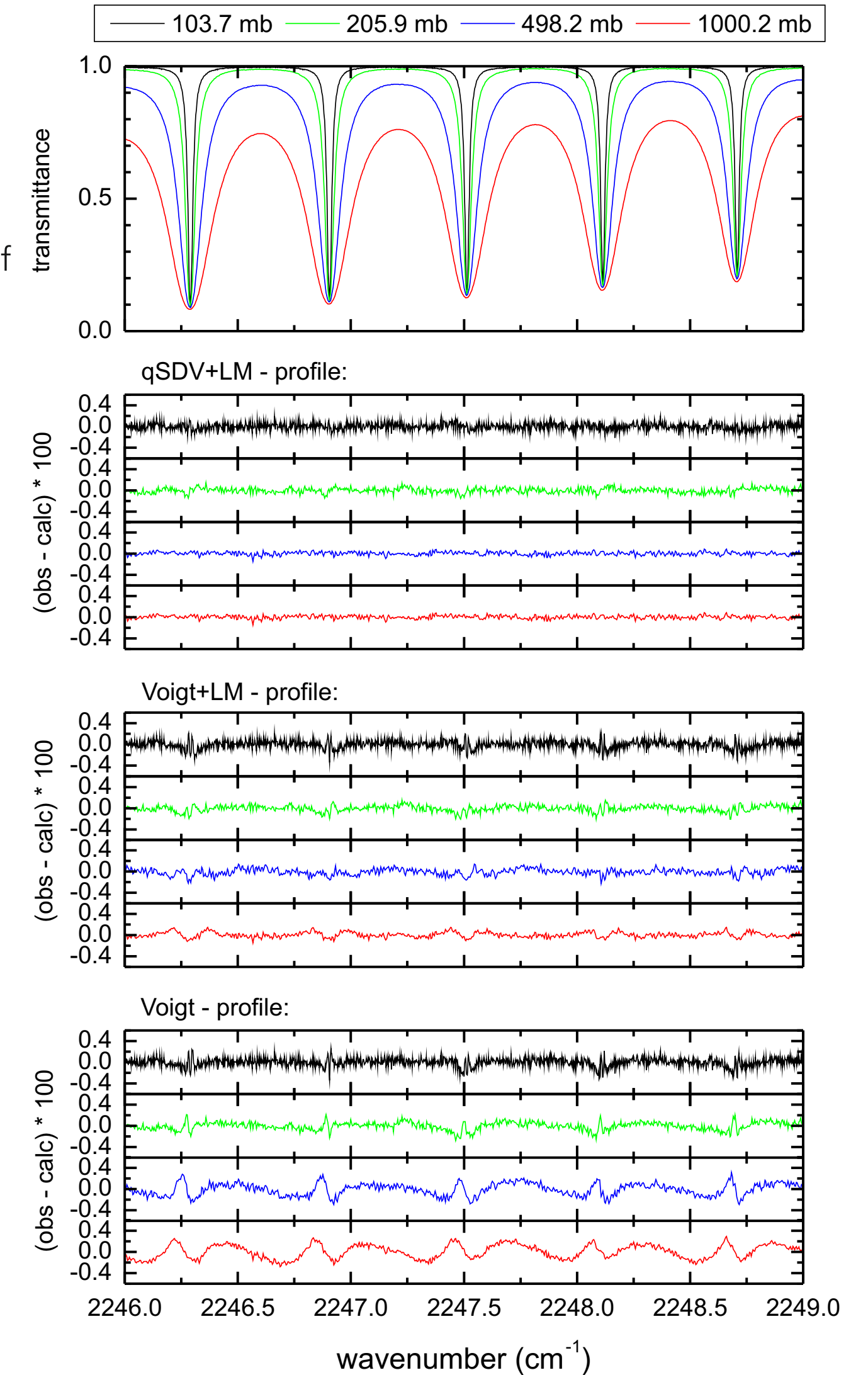


Fig. 2: Expanded segment ($31 \leq m \leq 35$) of the measured spectra and the resulting residuals shown in Fig. 1.

- parameters for air-broadening, speed dependence of width, air pressure shift and Rosenkranz line mixing were retrieved for $|m| \leq 40$ ($m=J''$ and $m=J''+1$ for the P and R branch, respectively)
- the parameters show a smooth dependence on m and were fitted using polynomial functions
- the smoothing functions should not be extrapolated and only be used inside the fitting range

Pressure shifts

- Clear deviations of shift parameters from HITRAN2012, especially in the P branch
- HITRAN values based on empirical expression linear in $|m|$ and line position [6]

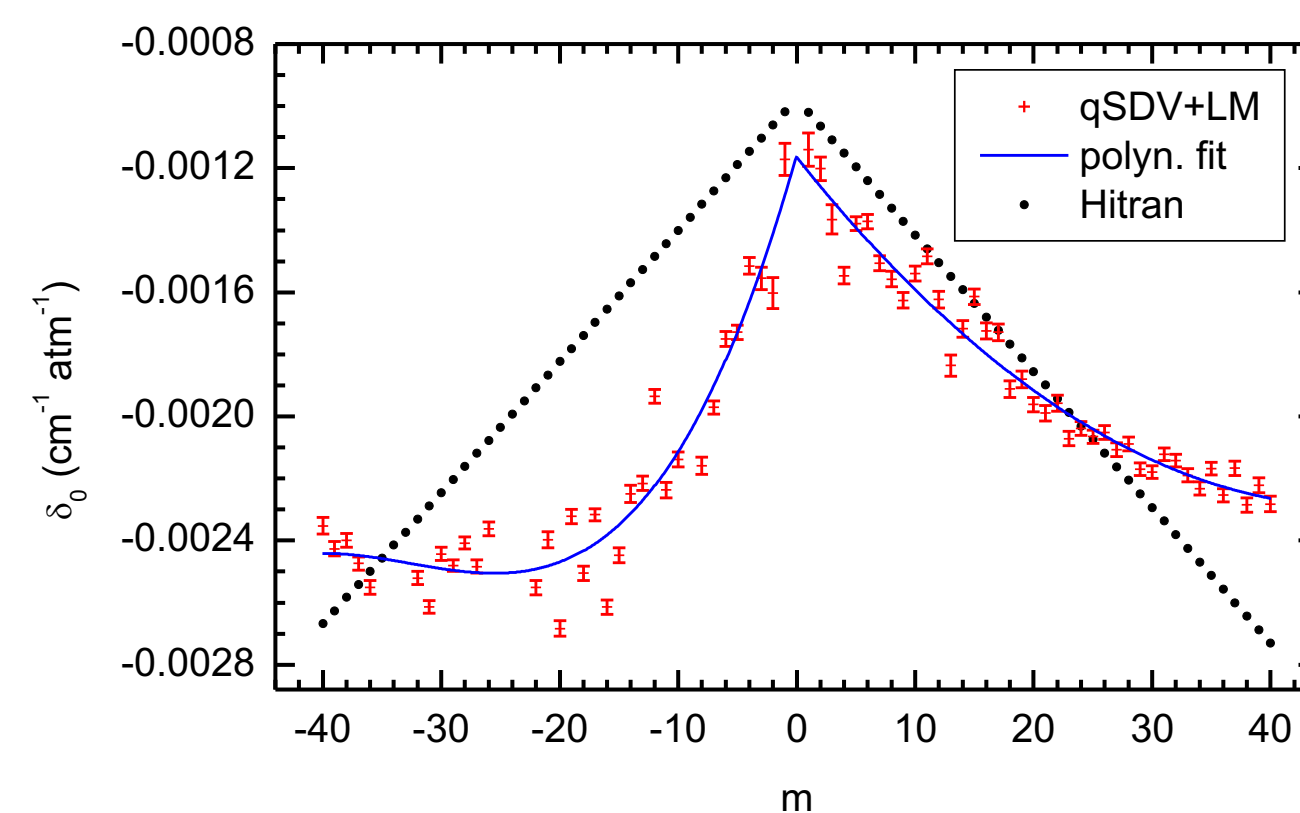


Fig. 6: Pressure shift parameter vs. m quantum number

Rosenkranz line mixing

- First measurement of line mixing in N_2O ν_3 band
- P and R branch show qualitatively the same behavior
- Sign of mixing parameter changes at the line with the highest intensity
- > Intensity is transferred from weak to strong lines

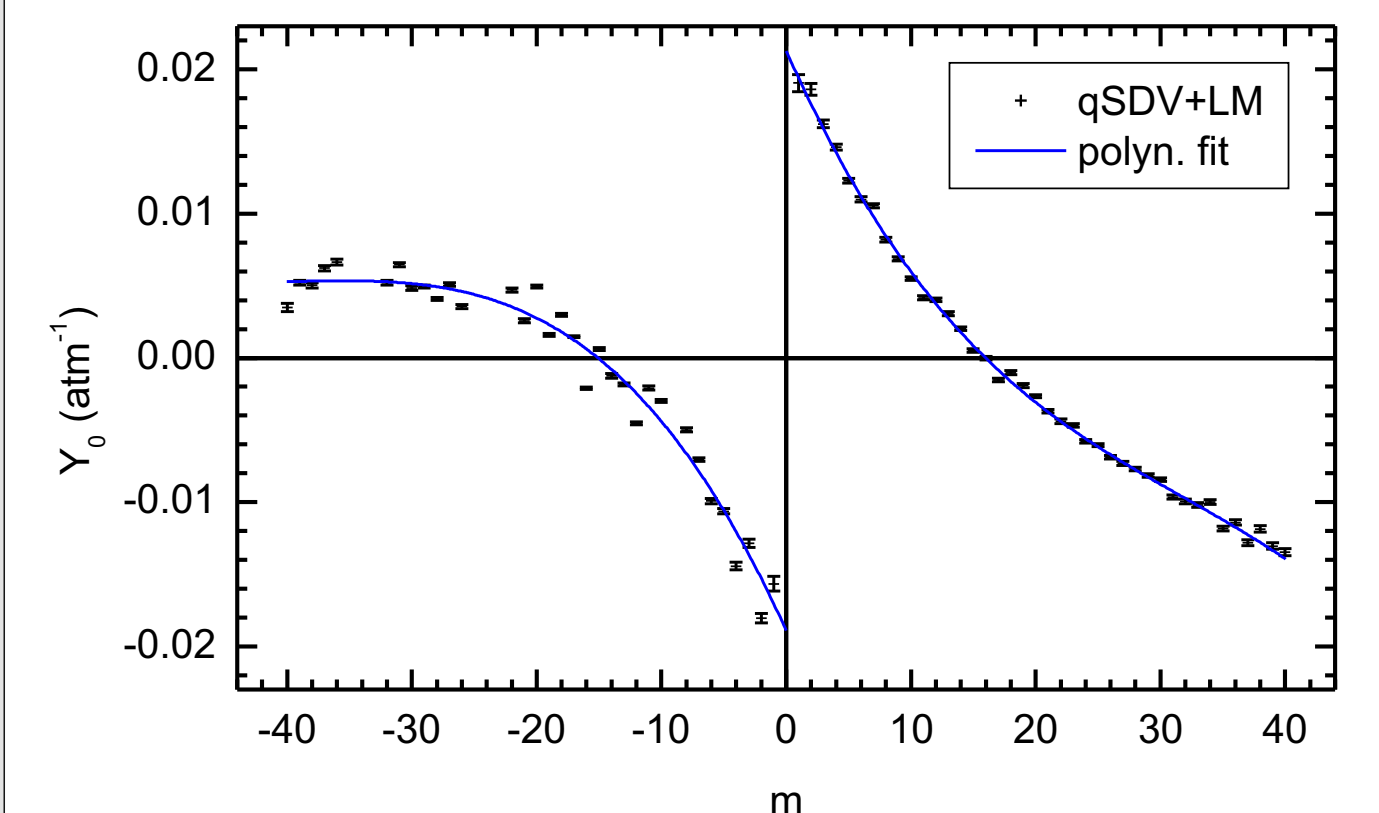


Fig. 7: Rosenkranz line mixing parameter vs. m quantum number

Pressure broadening and its speed dependence

- Smooth m -dependence of γ_0 and γ_2
- γ_0 values differ systematically from HITRAN2012 for all used line shape models
- Differences between HITRAN values and γ_0 from analyses without SD show strong dependence on optical depth
- SD is not accounted for in the analyses gone into HITRAN
- Effect of SD is largest near the line center, its influence decreases with increasing optical depth
- γ_0 values are commonly retrieved with the Voigt model and optically thin lines, resulting parameters are „effective“
- > γ_0 values from Voigt analyses should not be used for extrapolation in optical depth

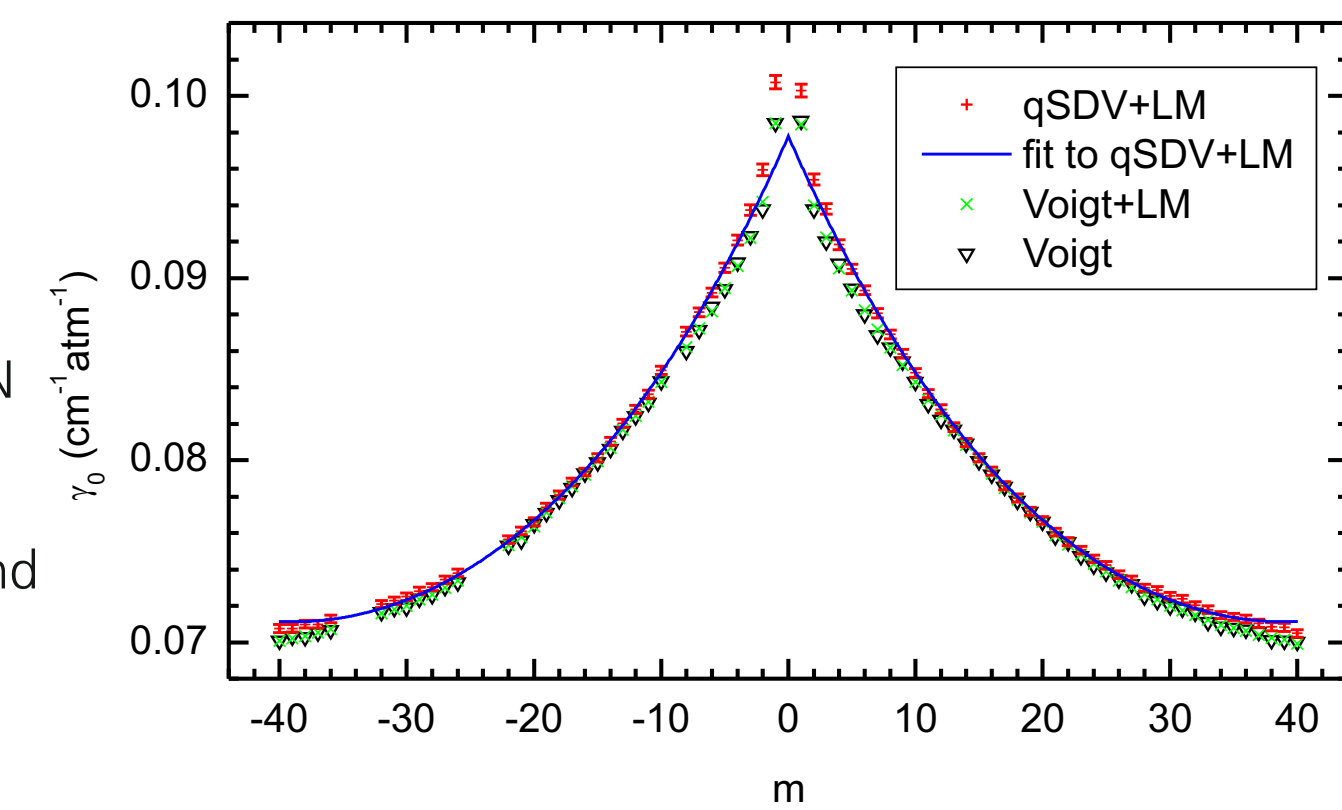


Fig. 3: Broadening parameters vs. m quantum numbers

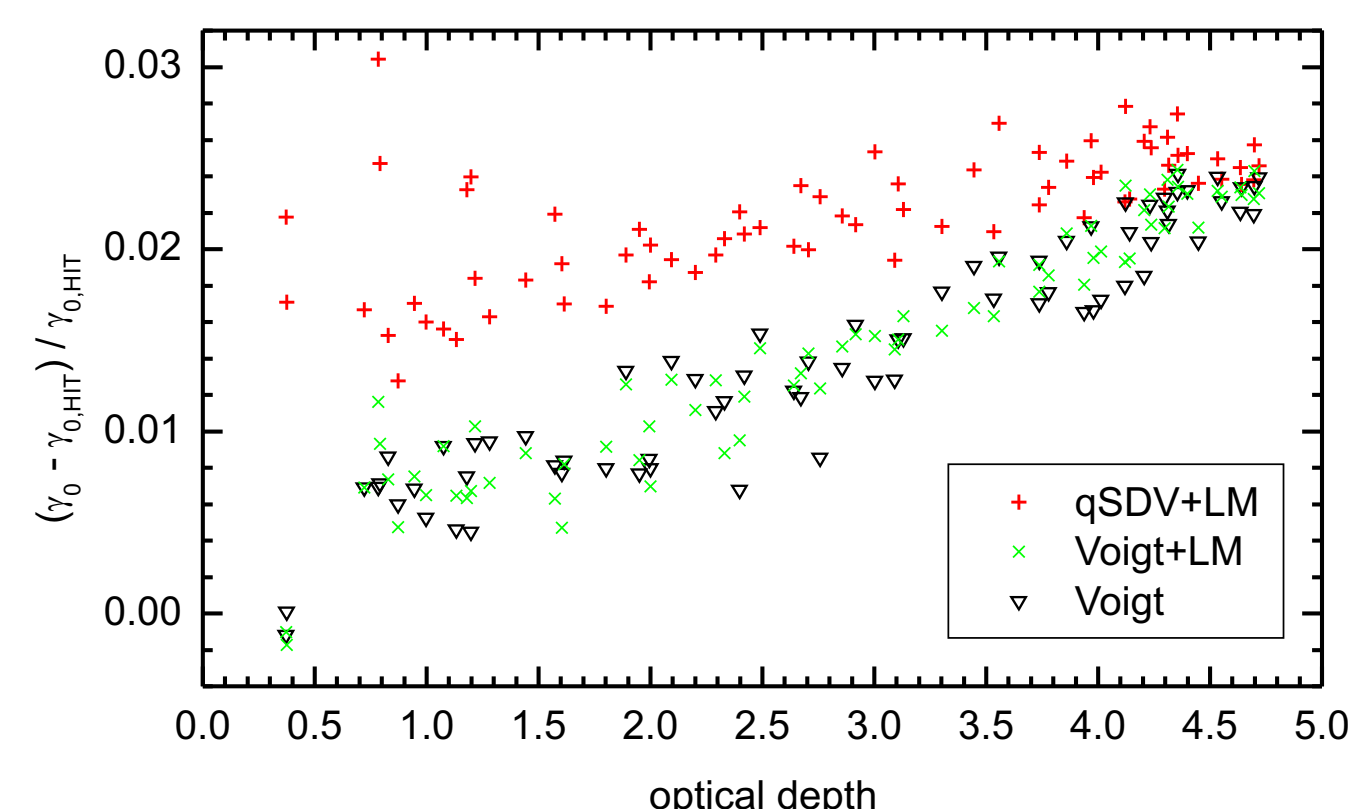


Fig. 4: Deviations of retrieved line broadening parameters from HITRAN2012 vs. the lines' optical depths.

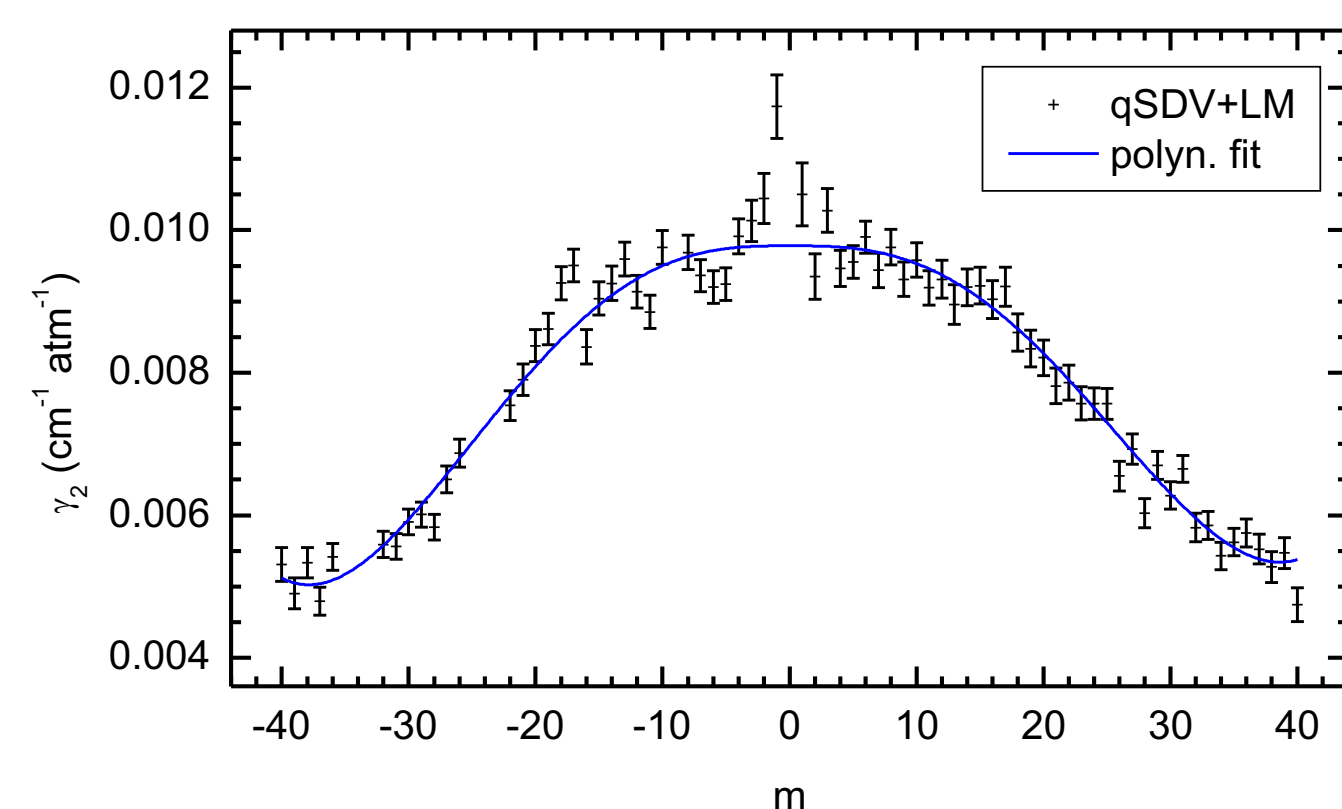


Fig. 5: Speed dependence parameter vs. m quantum number

Test of a more physical model

- Setting $\delta_0 = \nu_{VC,0} = \eta = 0$ is adequate for this set of measurements
- Dicke narrowing + SD might be visible in an extended measurements set
- Two spectral segments ($4 \leq m \leq 7$ and $31 \leq m \leq 35$) were refitted with theoretical $\nu_{VC,0}$
- The binary diffusion coefficient D was estimated at 296 K and 1 atm assuming a Lennard-Jones (6-12) potential
- ν_{VC} needs to be reduced by fitting η for optimum χ^2
- Δ_2 was constrained in order to reduce the consequential asymmetry caused by the same η for width and shift

Results

- No visible differences in the residuals compared to the fit using the qSDV+LM model
- χ^2 is reduced by about 1%
- γ_0 does not differ significantly, γ_2 shows an offset of 0.0011 cm^{-1} , δ_0 is increased by 2.7% on average
- Mean value for η is 0.32
- Correlation between Δ_2 and Y leads to a maximum deviation of Y of 2%
- A more rigorous test would require an extended high SNR set of measurements of lines not showing line mixing

$$\nu_{VC,0} = \frac{k_B T}{2\pi c m D}$$

$$\frac{\Delta_2}{\Delta_0} = \frac{\Gamma_2}{\Gamma_0}$$

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Deutsches Zentrum
für Luft- und Raumfahrt
German Aerospace Center